



TITLE:

# Pathways to Engineered Colloidal Crystals(Soft Matter as Structured Materials)

AUTHOR(S):

Ziherl, P.

---

CITATION:

Ziherl, P.. Pathways to Engineered Colloidal Crystals(Soft Matter as Structured Materials).  
物性研究 2005, 84(6): 846-847

ISSUE DATE:

2005-09-20

URL:

<http://hdl.handle.net/2433/110339>

RIGHT:

# Pathways to Engineered Colloidal Crystals

Dept. of Physics, University of Ljubljana, Slovenia

P. Ziherl<sup>1</sup>

J. Stefan Institute, Slovenia

Understanding order in colloidal systems has been an outstanding and multifaceted problem in soft matter physics for a long time. Even in a system as simple as monodisperse hard spheres, it took a microgravity experiment [1] to prove that at large enough densities they form a face-centered cubic (FCC) crystal as predicted theoretically rather than the glassy phase which is often observed in an Earth-based laboratory. In the recent years, it became clear that ordered colloids could be very useful in a number of applications; the most important examples include photonic crystals, microsieves, chemical reactors, and lightweight structural materials. In many of these systems it is desirable if not necessary that their space group be different from the FCC lattice to achieve the desired optical, mechanical or morphological properties.

In one of the first systematic experimental studies of non-FCC colloidal crystals, a body-centered cubic (BCC) lattice has been identified in charge-stabilized polystyrene spheres [2], which was consistent with the theoretical analysis of the phase diagram of point particles interacting with screened electrostatic repulsion [3]. Since then, many non-close-packed crystal lattices have been ascertained, some of them as exotic as the A15 or sigma phase [4], and reversible phase transitions between them have been observed [5]. All of these more complicated crystal structures were formed by nano-scale colloids, mostly self-assembled micellar aggregates of macromolecules such as dendrimers or block copolymers. This clearly indicates how important are the details and the exact shape of the interparticle potential: in micron-sized colloids, the pair potential is much more generic and hard to tune.

On the theoretical side, the problem has received considerable attention too. Given that there is no complete theoretical description of the crystalline state, the main tool used is the numerical simulation, which has produced some remarkable results. On the one hand, there are simulations of systems with realistic pair potentials, such as the ultra-soft logarithmic interaction of solutions of star polymers which have been predicted to exhibit FCC, BCC, body-centered orthorhombic, simple cubic, and diamond phases [6]. These studies can be used to establish direct connection to experiments, and some of them actually include molecular details at the atomic level [7]. On the other hand, many simulations have been performed on particles interacting with idealized model potentials [8] which typically include a hard core with an additional short-range interaction. Studies of model potentials have yielded several of the more conventional

---

<sup>1</sup>E-mail: primoz.ziherl@ijs.si

crystalline phases as well as lattices with elements of quasicrystalline order and structures with partial positional order. In view of providing guidance for experimentalists and chemists, such investigations are invaluable as they can separate the different properties of the potential to elucidate their role in stabilization of the non-close-packed lattices.

Another approach to the synthesis of the numerical and theoretical insight is to adopt a phenomenological point of view. This perspective has complemented the well-known close-packing rule (stating that the FCC lattice is the most stable arrangement of hard spheres because it has the largest packing fraction) by the opposing minimal-area rule that embodies the role of the soft repulsive tail of the pair potential and suggests that this tail stabilizes lattices such that their Voronoi partitions have the smallest area [9]. Presently, the A15 phase seems to be the minimal-area lattice, and the BCC lattice is somewhere between the FCC and A15 lattice. — This heuristic approach, which has been substantiated by more detailed studies and not found inconsistent with any reported experimental observation, can be used to estimate the symmetry of a certain system and could thus be of considerable assistance to experimentalists and chemists, especially in the preliminary phase of a study.

Currently, it appears that the research and development in the field of colloidal crystals is spearheaded by the numerical studies. Hopefully the most interesting pair potentials can be realized using the rapidly advancing methods of synthetic chemistry of macromolecules to produce novel and potentially useful colloidal crystalline phases.

## References

- [1] Z. Cheng et al., Phys. Rev. Lett. **88** (2002), 015501.
- [2] E. B. Sirota et al., Phys. Rev. Lett. **62** (1989), 1524.
- [3] K. Kremer, M. O. Robbins, and G. S. Grest, Phys. Rev. Lett. **57** (1986), 2694.
- [4] G. Ungar et al., Science **299** (2003), 1208.
- [5] T. P. Lodge et al., Phys. Rev. Lett. **92** (2004), 145501.
- [6] N. Hoffmann, C. N. Likos, and H. Löwen, J. Chem. Phys. **121** (2004), 7009.
- [7] Y. Li, S.-T. Lin, and W. A. Goddard III, J. Am. Chem. Soc. **126** (2004), 1872.
- [8] See, e.g., G. Malescio and G. Pellicane, Nature Materials **2**, 97 (2003).
- [9] P. Ziherl and R. D. Kamien, J. Phys. Chem. B **105** (2001), 10147.